Water Research 163 (2019) 114858

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Persistent contaminants as potential constraints on the recovery of urban river food webs from gross pollution

Fredric M. Windsor[a, b, *, 1], M. Glória Pereira[c], Charles R. Tyler[b], Steve J. Ormerod[a]

[a] School of Biosciences, Cardiff University, UK
[b] Department of Biosciences, University of Exeter, UK
[c] Centre for Ecology and Hydrology, Lancaster, UK

ARTICLE INFO

Article history:
Received 9 March 2019
Received in revised form
12 July 2019
Accepted 12 July 2019
Available online 13 July 2019

Keywords:
Biodiversity
Ecosystems
Food webs
Functional diversity
Macroinvertebrates
Persistent organic pollutants

ABSTRACT

Urban areas contribute substantially to xenobiotic contaminant loads in rivers, but their effects have been investigated more for individual organisms and sensitive taxa, rather than through the emergent properties of communities. Here, we use replicated, catchment-scale sampling of benthic invertebrates and novel multivariate techniques to assess whether urban wastewater contaminants affected the structure and function of river food webs. We postulated that the continued occurrence of selected contaminants in river systems might explain the incomplete recovery of urban rivers from legacy gross pollution. Benthic invertebrate communities were sampled monthly over a year (2016–2017) at 18 sites across 3 river systems in South Wales (United Kingdom). Contaminant sources were characterised using remote sensing, water quality data from routine monitoring and measured concentrations of selected persistent xenobiotic pollutants (polychlorinated biphenyls and polybrominated diphenyl ethers). Urban wastewater discharges had relatively limited effects on river water quality, with small increases in nitrate, phosphate, temperature, conductivity and total dissolved solids in urban systems. Concentrations of polychlorinated biphenyls and polybrominated diphenyl ethers in invertebrates, however, were significantly higher under greater urban land cover and wastewater discharge. Food webs at the most highly contaminated urban sites were characterised by: (i) reduced taxonomic and functional diversity; (ii) simplified food web structure with reduced network connectance; and (iii) reductions in the abundance of prey important for apex predators such as the Eurasian dipper (*Cinclus cinclus*). Although correlative and partially confounded by other effects, these data provide support for the hypothesis that impairment to food webs resulting from urban pollutants might explain population, community and ecosystem-level effects in urban river systems, and hence incomplete recovery from past pollution.

1. Introduction

Urban landscapes across the world are linked with effects on water quantity and reduced quality that reflect factors such increased population density, waste disposal, flow modification, river habitat modification and increased water temperatures (Dudgeon et al., 2006; Zimmerman et al., 2008; Reid et al., 2018). Among these effects, water pollution is one of the most pervasive, and has recognised detrimental impacts on river biota (Harding et al., 1998; Moss, 2008; Relyea, 2005; Schulz, 2004) while also representing risks to human health (Schwarzenbach et al., 2010).

A large number of pollutants reach river systems from point and diffuse sources (Walsh, 2000; Bester et al., 2008; Heeb et al., 2012), and in urban systems these include impervious urban surfaces, stormwater systems, wastewater treatment works (WwTWs), combined sewage overflows and industry discharges (Pitt et al., 1995; Feng et al., 1998; Phillips et al., 2012; Krein et al., 2013). Wastewaters are typically dominated by organic compounds, sediments and nutrients, but they also contain low levels of xenobiotic chemicals, such as pharmaceuticals, as well as other pollutants that reach sewers from surface drains. Discharges from industry depend on the specific processes involved, but often involve low concentrations of toxic substances either of emerging concern or 'legacy' pollutants such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) or non-brominated flame

* Corresponding author. School of Biosciences, Cardiff University, UK.
E-mail address: fredric.windsor@newcastle.ac.uk (F.M. Windsor).
[1] Present address: School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, UK.

https://doi.org/10.1016/j.watres.2019.114858

retardants (Fu et al., 2003; Owens et al., 2001). For all urban pollution sources, the relative discharge and chemical composition is inherently dependent upon population density, demography and the types of anthropogenic activity within the upstream contributing catchment (Taebi and Droste, 2004). Consequently, areas with high population density and high urban land cover contribute most effluent and xenobiotic pollutants as a proportion of river runoff, thus also potentially generating the largest ecological effects (Dyer and Wang, 2002).

The effects of anthropogenic contaminants on individual organisms are relatively well understood and include mouthpart deformities, reduced reproductive capability and increased mortality (see Colborn et al., 1993; Jobling et al., 1998; Tyler et al., 1998; Watts et al., 2003; Segner et al., 2003). At higher levels of biological organisation, however, understanding of chemical effects is more restricted (Gavrilescu et al., 2015; Petrie et al., 2015; Windsor et al., 2018). Specifically, there is a need for research assessing the effects of xenobiotic chemicals across communities and food webs to understand more accurately the risk of these pollutants in natural systems (Windsor et al., 2018).

Assessing the effects of pollutants in the field is not straightforward and requires some understanding of the changing context in which urban pollution is managed. The systematic regulation of conventional and toxic pollutants through national and European Union directives (e.g. Urban Wastewater Treatment Directive 91/271/EEC; Water Framework Directive, 2000/60/EC), alongside advances in urban water treatment, have led to significant reductions in the concentration of hazardous organic compounds within the UK and across Europe (Eggen et al., 2014). In particular, improvements in contemporary sewage treatment, such as the growing use of activated sludge processes, has enabled the more effective removal of organic matter, nitrate, phosphate, suspended sediments and many contaminants from effluents (Ahmed et al., 2017; van Loosdrecht and Brdjanovic, 2014). Subsequently, there have been improvements over recent decades in water quality and biological diversity in rivers downstream of urban areas – at least in western Europe (Brosnan and O'Shea, 1996; Vaughan and Ormerod, 2012). In spite of these improvements, a range of contaminants still persist in urban runoff at low, but toxic, concentrations (Blackburn and Waldock, 1995; Purdom et al., 1994; Zhou et al., 2009). Moreover, biological recovery from the effects of past insanitary pollution is still only partial in England and Wales, with rivers in urban location still supporting only 60% of the macroinvertebrate families found in non-urban catchments (Vaughan and Ormerod, 2012). Parallel evidence suggests also that toxic substances might now affect clean-water organisms, such as the Eurasian dipper (*Cinclus cinclus*), that are recolonising formerly polluted urban river systems (Morrissey et al. 2013a,b, 2014). We looked to assess whether similar effects might explain the current status and incomplete recovery of communities of river organisms, or the food webs of which they constitute, from past pollution.

Specifically, we aimed to assess the putative effects of persistent xenobiotic pollution on the structure and function of riverine macroinvertebrate communities and food webs, as a potential explanation for the incomplete recovery of urban rivers in Britain from past insanitary pollution (Vaughan and Ormerod, 2012). Within this over-arching hypothesis we predicted that:

1. Food web structure will relate to the levels of urban wastewater contamination in river systems
2. The ecological function of river food webs, defined by the diversity of biological traits, will be negatively related to the levels of urban pollution
3. Emergent effects resulting from changes in macroinvertebrate community and food web structure are present in urban river systems

2. Material and methods

2.1. Sample sites

Eighteen sites across South Wales were used to assess relationships between urban effluents on macroinvertebrate communities (Fig. 1). Sample sites were paired upstream or downstream of WwTWs and located across a gradient of urban land use (0.11–33.50 km^2) and other urban pollution point sources. Up- and down-stream sites were within ~1 km of one another and were selected to minimise differences in meso-habitat conditions between locations, for example substratum conditions, depth and current velocity.

Sites were situated across three hydrological catchments (Taff, Usk and Wye), each of which has a distinct land use history. The Taff catchment has historically supported heavy industrial activity, related to coal mining and gasification (Scullion and Edwards, 1980), and the area remains heavily urbanised. In contrast, the

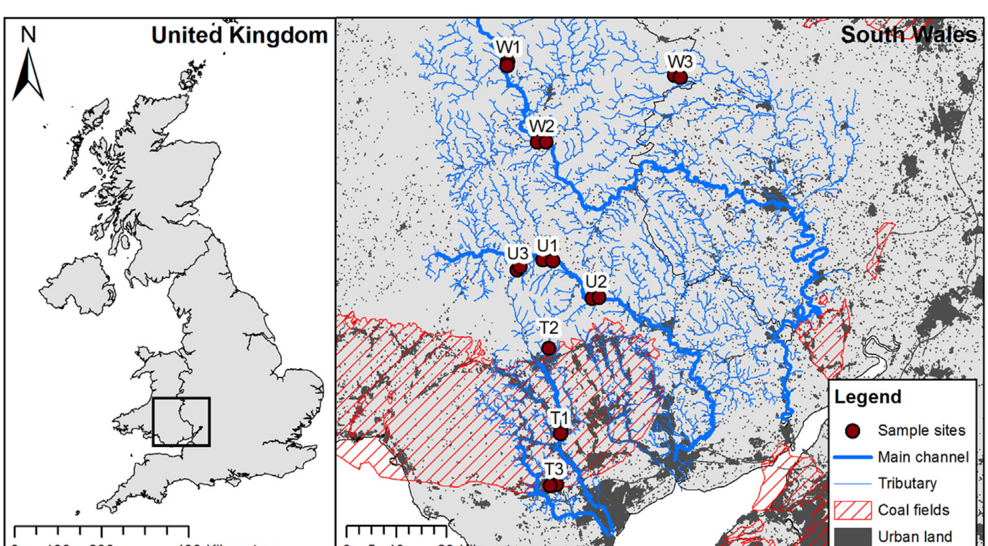

Fig. 1. A map of sample locations across South Wales. Site codes correspond to secondary data collated from a range of sources (Table 1).

Table 1
Physicochemical conditions adjacent to paired invertebrate sample sites across South Wales. Data are mean values (standard error) from EA and NRW datasets over the duration of invertebrate sampling (2015–2017).

Site	Urban (%)	Mean Ratio (E:R)*	Low-flow Ratio (E:R)*	Nitrate (NO_3^- mg/l)	Phosphate (PO_4^{3-} mg/l)	DO (mg/l)	HQA score	HM score	HM class	RQI score
T1	11.01	0.0109	0.0612	1.81 (0.11)	0.07 (0.01)	11.16 (0.22)	57	450	3	111
T2	0.34	0.0022	0.0083	0.25 (0.06)	0.05 (0.02)	11.27 (0.43)	58	125	2	118
T3	20.38	0.0032	0.0159	2.33 (0.43)	0.19 (0.06)	10.31 (0.10)	55	200	3	111
U1	1.14	0.0043	0.0368	0.92 (0.04)	0.05 (0.01)	11.63 (0.14)	62	10	1	109
U2	1.09	0.0002	0.0019	1.09 (0.10)	0.04 (0.01)	11.53 (0.13)	64	100	2	112
U3	0.97	0.0042	0.0398	0.80 (0.05)	0.03 (0.01)	11.67 (0.14)	63	50	2	113
W1	0.47	0.0045	0.0531	0.62 (0.04)	0.02 (0.01)	11.50 (0.19)	67	25	2	113
W2	0.01	0.0005	0.0042	0.65 (0.03)	0.03 (0.01)	11.57 (0.15)	65	50	2	109
W3	2.28	0.0034	0.0206	3.43 (0.10)	0.04 (0.01)	11.24 (0.16)	63	25	2	113

E:R = Ratio of WwTW effluent to river discharge for downstream sites. HQA = Habitat Quality Assessment; HM = Habitat Modification; RQI = Riparian Quality Index.

Usk and Wye catchments are more rural, with agricultural management practices dominating land use, typically livestock grazing. The inter-catchment differences in land use generate variation in the environmental conditions and allow for different ‘environmental contexts’ (Burdon et al., 2016).

Contributing land cover, including urban land (km^2), was determined for the upstream catchment of each sample site using JNCC phase 1 habitat classification data (JNNC, 2010), in conjunction with Spatial Tools for the Analysis of River Systems (STARS) and Spatial Stream Network (SSN) (Ver Hoef et al., 2014). Effluent discharge from WwTWs was recorded as the dry weather average (m^3 s^{-1}) collated from the regulatory consents from the Government sponsored regulator, NRW (© Natural Resources Wales and database right. All rights reserved). River discharge (m^3 s^{-1}) data were also collated from NRW river gauging stations proximal to the sample sites and summarised as the mean daily discharge over the monitoring period or as Q95 (low flow) (Appendix S1). At sites downstream of WwTWs the ratio of wastewater effluent to mean annual river discharge was highly variable, enabling a gradient of environmental conditions across the landscape (Table 1). Invertebrate communities across the catchments have a similar structure, dominated by Ephemeroptera, Plecoptera, Trichoptera, Diptera and Coleoptera typical of relatively base-rich stony streams, and are derived from a wider regional species pool present across South Wales (Appendix S2).

2.2. Physicochemical characterisation

A series of physicochemical variables were measured to assess the effects of urban land cover and wastewater effluent on the water quality of stream reaches. Monthly spot measurements of water temperature (°C), electrical conductivity (EC; µS/cm), Total Dissolved Solids (TDS; mg/l) and pH were used to assess changes in water chemistry in response to urban wastewater effluent, following previous practice (Igbinosa and Okoh, 2009). Water quality analyses (2015–2017) carried out by NRW (© Natural Resources Wales and database right. All rights reserved), were also used as environmental covariates to account for potential variation in other water quality metrics. One constraint was that these data were available only downstream of WwTWs because these specific NRW monitoring sites specifically monitor water chemistry downstream of urban areas and WwTW effluent discharges (Table 1 and Appendix S1).

To account for the potential confounding effects of physical conditions on invertebrates, including riparian cover, channel morphology and benthic sediment character, we used the River Habitat Survey (RHS; Raven et al., 1998) to generate a habitat quality (HQA) and modification score (HMS), as well as Riparian Quality Index (RQI), for each of the sample sites.

2.3. Chemical analyses

The concentrations of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were measured in invertebrates across sample sites downstream of urban areas and effluent discharges (n = 9). For the specific purposes of this paper, we use body burden data for PCBs and PBDEs to provide a spatio-temporally averaged measure of persistent contamination, with concentrations of bioaccumulative chemicals in organisms assumed to reflect long-term exposure concentrations (Schäfer et al., 2015). These chemicals have a high toxicity, are hydrophobic and partition into sedimentary/organic matter phases in freshwater environments leading to likely interaction with benthic invertebrates (Karickhoff et al., 1979). Over 2016 (May–September) benthic invertebrate taxa (Heptageniidae, Baetidae, Leuctridae, Hydropsychidae, Rhyacophilidae) were sampled. For each sample (n = 44), multiple individuals of each taxa (n = 50–200) were pooled to collect a 1–2 g of sample. Gas Chromatography Mass Spectrometry (GC/MS) was then used to quantify the concentration of PCBs and PBDEs in samples of each taxa across sites. The total concentration of PCBs and PBDEs (ng/g wet weight) was aggregated, and standardised based on the biomass of sampled invertebrates at each site (g m^{-2}; see Appendix S3), to provide a measure of the level of persistent contamination in the invertebrate food web (weighted ng/g ww). A full description of sample collection and analysis is provided in Appendix S3.

2.4. Macroinvertebrate community structure

Macroinvertebrate communities were characterised by three pooled Hess (1941) samples (165 cm^2, 500 µm mesh gauge) per sampling occasion at each site, intended to collect from the dominant benthic habitats present within each stream reach (Beisel et al., 1998). Samples were collected monthly over 2016–2017 and preserved on-site in 70% ethanol before subsequent sorting and identification macroscopically to the lowest practical taxonomic resolution (minimum of family, and species where possible). The final dataset comprised multivariate, community-level taxonomic data across the 18 sites. Taxonomic data were summarised using common metrics including species richness, total abundance and Simpson's index (SI = *1–D*) (Simpson, 1949). To assess any landscape-level taxonomic homogenisation of macroinvertebrate communities that occurs in response to WwTW discharges, the Chao index of similarity (Chao et al., 2005) was computed for independent pair-wise comparisons (upstream–upstream and downstream–downstream of effluent discharge points).

2.5. Macroinvertebrate community function

To parameterise macroinvertebrate communty function, we generated a functional dataset through linking taxonomic information to a series of fuzzy-coded trait data derived from the European trait database (Tachet et al., 2002). These data were also supplemented by non-fuzzy, categorised feeding guild data for macroinvertebrate taxa of the South Wales (I Durance & S J Ormerod, Unpublished data). This dataset was used to understand trait variation in response to urban land cover and effluent discharges, but also to calculate the functional diversity of communities. For each community we calculated inter-taxon functional metrics, with this approach being preferred over the mean-taxon method due to risks in the latter of systematic and detrimental exclusion of important within-taxon functional trait variability (Violle et al., 2012). Our approach followed Gutiérrez-Cánovas et al. (2015) in that a subset of traits related urban land cover and effluent concentrations were selected based on the values of individual Pearson correlations. Traits with an average absolute coefficient of $R \geq |0.40|$ were included for the calculation of functional diversity. For the sub-set of selected traits, assessments of inter-taxon functional diversity were completed by defining a multidimensional Euclidean space, where axes summarised variation in traits. Subsequently, taxon functional richness (tFRic), as well as community functional richness (FRic), dispersion (FDis), similarity (FSim) and redundancy (FRed), were calculated at sample sites. Specific definitions of these functional metrics are provided in Appendix S4.

2.6. Macroinvertebrate food webs

Food webs for each sample site were constructed from pooled annual macroinvertebrate data, using computational methodology outlined in Gray et al. (2015) based on an R function, WebBuilder, in conjunction with the 'cheddar' package (Hudson et al., 2013). The method used community data in conjunction with a reference dataset of ~20,000 freshwater trophic interactions (Brose et al., 2005; Gray et al., 2015). Quantitative network metrics were calculated to describe food web structure; connectance, link density, mean chain length, generality (number of resources per consumer) and vulnerability (number of consumers per resource) (Bersier et al., 2002).

2.7. Statistical analyses

The potential effects of urban contamination on the structure and function of macroinvertebrate communities were investigated using 'R' statistical software (version 3.2.3) (R Core Team, 2015). Prior to further analysis data were explored following Zuur et al. (2010) to check for normality, heteroscedasticity and outliers in the data, and to select statistical tests.

Generalised Linear Models (GLMs) and Generalised Linear Mixed Models (GLMMs), the latter fitted using the package 'lme4' (Bates et al., 2015), were used to assess the relationships between taxonomic and functional diversity, food web characteristics and urban pollution. Where required, 'catchment' was included as a random effect to account for broad-scale biogeographical patterns of species distribution (Grönroos and Heino, 2012). From broad model structures, including a wide range of candidate variables (arable land cover, urban land cover, water temperature, total dissolved solids, WwTW effluent discharge), model selection was completed using both shrinkage and backward selection methods (Marra and Wood, 2011). Validation procedures, following Zuur et al. (2007) and Thomas et al. (2015), were used to assess the validity and robustness of statistical analyses. For each model, residual normality was assessed using QQ plots, homogeneity of variance was determined by plotting residuals against fitted values, and influential observations were investigated using Cook's leverage distances.

Chao index values were non-normal, yet sample sizes were equal and between-group variance was homogenous, thus Kruskal-Wallis rank sum tests (Ruxton and Beauchamp, 2008) were selected for analysis.

Multivariate analyses were used to assess invertebrate community structure and function. Non-metric Multidimensional Scaling (NMDS) ordination was utilised to visualise the multivariate relationships. NMDS was computed using the Jaccard index (Jaccard, 1908) with a square root transformation and Wisconsin double standardisation to account for variation associated with both common and rare taxa within the dataset (Kenkel and Orloci, 1986). Multivariate GLMs, constructed using the "mvabund" package (Wang et al., 2012), were used to assess taxonomic responses and identify the dominant species contributing to observed patterns. The relationships between macroinvertebrate community function and urban pollution sources were assessed using R-mode linked to Q-mode (RLQ) and fourth-corner analysis, following Dray et al. (2014). This allowed for links to be drawn between species, trait and environmental datasets. A modelling framework was not used to combine RLQ with fourth-corner analysis (see ter Braak et al., 2017). Multivariate methods, taxonomic and functional metrics were applied to assess the responses of food webs to urban pollution.

3. Results

3.1. Community structure along a gradient of urban land cover

Macroinvertebrate diversity was related to both urban land-cover and WwTW discharges ($R^2c = 0.76$, $F_{7,180} = 319.41$, $p < 0.001$). Taxonomic diversity was negatively related to the urban land cover upstream of sample sites (-0.029 ± 0.001 SI per %; $F_{1,180} = 23.45$, $p < 0.001$). Reductions in diversity were also related significantly to the ratio of effluent to river discharge (i.e. increased effluent concentration) ($F_{1,180} = 3.67$, $p = 0.003$). Interestingly, urban land cover and WwTW discharge interacted to affect diversity ($F_{1,180} = 3.32$, $p = 0.001$), with SI values lowest at sites with greater urban land cover and higher levels of wastewater discharge from WwTWs (Fig. 2).

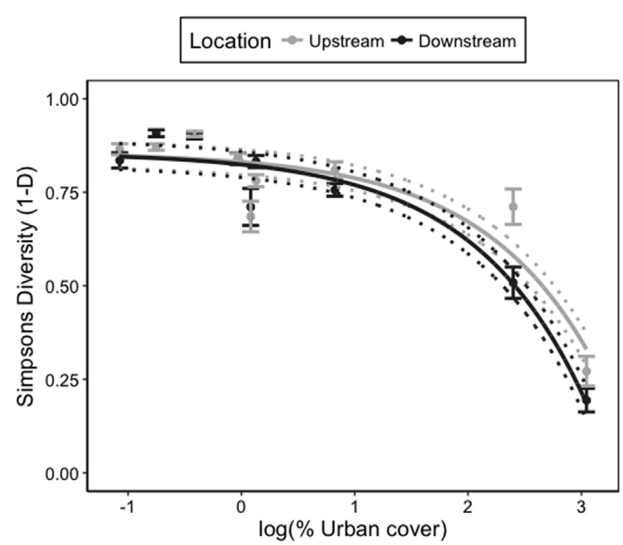

Fig. 2. Relationship between macroinvertebrate taxonomic diversity and $\log^e$ percentage urban area upstream. Data points are mean annual values upstream and downstream of WwTW discharges (2016–2017). Error bars and dotted lines are ±1 standard error. The relationship was derived from a GLMM ($R^2 = 0.76$, $F_{1,180} = 3.32$, $p = 0.001$), with statistics in text.

Table 2
Taxon-specific contributions to changes in invertebrate community structure along a gradient of increasing urban land cover.

Taxon	Effect[a]	Deviance	*P*-value
Gammarus pulex/fossarum	+	90.55	0.001
Rhithrogena semicolorata	−	58.29	0.001
Tubificidae spp.	+	33.90	0.001
Ancylus fluviatalis	−	27.49	0.001
Amphinemura sulcicollis	−	26.10	0.001
Leuctra moseyli/hippopus	−	21.06	0.004
Limnius volckmari	−	18.65	0.007
Glossosoma conformis	−	18.41	0.007
Agapetus fuscipes	−	17.17	0.010
Baetis rhodani	−	15.16	0.013
Esolus parallelepipedus	−	14.82	0.017
Leuctra inermis	−	14.77	0.017
Sericostoma personatum	−	14.39	0.020
Protonemoura meyeri	−	13.90	0.021
Hydroptila spp.	−	13.66	0.024
Hydropsyche siltalai	−	13.57	0.026

[a] Direction of change in the relative abundance of taxa.

Several taxa varied in abundance along the gradient of urban land cover (Table 2). Community structure measured from non-metric multi-dimensional scaling reflected urban land cover and wastewater discharges ($LR_{14,201} = 3203.00$, $p < 0.001$; see Fig. 3), with effects seen both individually (Urban land cover $LR_{1,213} = 615.00$, $p < 0.001$; WwTW discharge $LR_{1,214} = 168.10$, $p = 0.002$) and with an interaction ($LR_{1,201} = 107.7$, $p = 0.037$). Community structure also differed upstream and downstream of WwTW discharges, particularly at the most urbanised locations, where there was greater than 10% urban land in the upstream catchment (e.g. T1 and T3). Community structure also varied among sample dates, as expected from seasonal changes ($LR_{11,202} = 2312.10$, $p < 0.001$).

Although there were no significant differences in the structure of food webs and occurrence of trophic interactions upstream and downstream of WwTWs, there were significant relationships between food web character and urban land cover (Fig. 4). Connectance was relatively poorly explained by urban land cover and WwTWs ($R^2 = 0.16$, $t_{3,14} = 0.89$, $p = 0.47$). All other models, including both urban land cover and wastewater discharges, explained variation in quantitative food web metrics, including; link density ($R^2 = 0.97$, $t_{3,14} = 266.00$, $p < 0.001$), mean chain length ($R^2 = 0.91$, $t_{3,14} = 54.67$, $p < 0.001$), generality ($R^2 = 0.98$, $t_{3,14} = 293.20$, $p < 0.001$) and vulnerability ($R^2 = 0.97$, $t_{3,14} = 202.00$, $p < 0.001$). Within these models link density ($t_{1,14} = -3.36$, $p = 0.005$), mean chain length ($t_{1,14} = -3.35$, $p = 0.003$), generality ($t_{1,14} = -3.30$, $p = 0.005$) and vulnerability ($t_{1,14} = -3.11$, $p = 0.007$) were negatively related to urban land cover but not significantly related to the level of effluent discharge.

Macroinvertebrate communities downstream of urban wastewater discharges were more similar to one another than compared with those of upstream sites ($\chi^2_{1,5776} = 9.56$, $p = 0.002$; Kruskal Wallis rank sum test); downstream sites had consistently lower Chao index values. Although statistically significant, the mean similarity of downstream communities (0.38 ± 0.0028) was only marginally lower than found for upstream communities (0.39 ± 0.0027).

3.2. *Community function along a gradient of urban land cover*

The functional character of macroinvertebrate communities was related to both urban land cover and WwTW discharges (Fig. 5). Although variable in power, all models explained significant variation in functional diversity metrics, including FSim ($R^2 = 0.41$, $F_{3,212} = 48.97$, $p < 0.001$), tFRic ($R^2 = 0.30$, $F_{3,212} = 29.61$, $p < 0.001$), FRic ($R^2 = 0.15$, $F_{3,212} = 12.56$, $p < 0.001$), FDis ($R^2 = 0.29$, $F_{3,212} = 30.29$, $p < 0.001$) and FRed ($R^2 = 0.19$, $F_{3,212} = 17.43$, $p < 0.001$). Of particular note, FSim increased markedly in relation to increasing urban land cover ($t_{1,212} = 10.87$, $p < 0.001$), particularly downstream of WwTW effluent discharges ($t_{1,212} = 4.44$, $p < 0.001$). In contrast, FRic decreased with urban land cover ($t_{1,212} = -5.36$, $p < 0.001$), again most clearly seen for sites downstream of WwTW discharges ($t_{1,212} = -2.99$, $p = 0.003$).

Relationships between macroinvertebrate functional traits and environmental variables are also apparent in RLQ analyses. Specifically, organisms preferring gravel substrata were not favoured downstream of WwTW discharges (-2.02 ± 0.04, $p = 0.024$). Aerial dispersing (-1.71 ± 0.29, $p = 0.019$) and uni-voltine taxa (-1.72 ± 0.30, $p = 0.02$) both decreased with urban land cover while the abundance of taxa with gills for respiratory processes was higher (1.51 ± 0.31, $p = 0.041$).

3.3. *Water quality and contaminants along an urban gradient*

Physicochemical conditions of the riverine sites varied moderately across sites: water temperature (10.89 ± 3.46 °C; $R^2c = 0.89$, $F_{7,200} = 42.11$, $p < 0.001$), TDS (66.53 ± 21.72 ppm; $R^2c = 0.53$, $F_{7,170} = 13.68$, $p = 0.007$) and EC (230.91 ± 40.98 μS/cm; $R^2c = 0.53$, $F_{7,170} = 13.50$, $p = 0.009$) were explained by wastewater discharges and urban land cover, in conjunction with month of sample collection. EC and TDS were both higher downstream of WwTWs ($F_{1,170} = 5.10$, $p = 0.03$; $F_{1,170} = 4.98$, $p = 0.03$; respectively) and water temperature was higher in urbanised sites ($F_{1,200} = 44.06$, $p < 0.001$). Total nitrate (NO_3^-) varied among sampled sites, with patterns also reflecting urban land cover and effluent discharge ($R^2 = 0.13$, $F_{3,67} = 3.32$, $p = 0.025$). Concentrations of NO_3^- were unrelated to urban land cover *per se* ($t_{1,67} = 0.47$, $p = 0.64$), but were higher with higher levels of urban land cover in combination with greater contributions to runoff from effluent discharge ($F_{1,67} = 2.03$, $p = 0.047$). Phosphate concentrations (PO_4^{3-}) were highly variable, and as a result were not significantly related to urban land cover or effluent discharge from WwTWs despite moderately higher values under urban land cover ($R^2 = 0.01$, $F_{3,65} = 0.31$, $p = 0.817$).

There was limited evidence for changes in river habitat quality with increasing urbanisation. Levels of riparian quality (RQI) were not significantly related to urban land cover or the presence of WwTW discharges ($R^2 = 0.04$, $F_{2,15} = 1.31$, $p = 0.299$). Habitat modification scores were shown to vary across the sites ($R^2 = 0.44$, $F_{2,15} = 7.76$, $p = 0.005$), with moderate increases in urban systems ($F_{1,15} = 3.91$, $p = 0.001$) yet no difference observed between sites upstream and downstream of WwTW discharges ($F_{1,15} = 0.51$, $p = 0.623$). Habitat quality exhibited a negative relationship with urban land cover ($R^2 = 0.45$, $F_{1,16} = 14.76$, $p = 0.002$), although in actual terms this reduction was relatively minor (54–68) and, based on benchmarking in the RHS protocol, these differences are considered small, and sites would be classed as near-identical.

The concentrations of xenobiotic pollutants (PCBs and PBDEs), measured in invertebrate communities (3.76–291.31 weighted ng/g ww), in the river systems were related to urban land cover and WwTW discharges across sample sites ($R^2 = 0.45$, $F_{6,55} = 6.94$, $p = 0.05$), with total PCB and PBDE concentrations greater under urban land cover ($t_{1,55} = 2.14$, $p = 0.037$). Effects were combined with higher relative contributions of effluent, such that highly urbanised sites with low dilution rates of WwTW effluent had the highest PCB and PBDE concentrations ($t_{1,55} = 1.94$, $p = 0.057$).

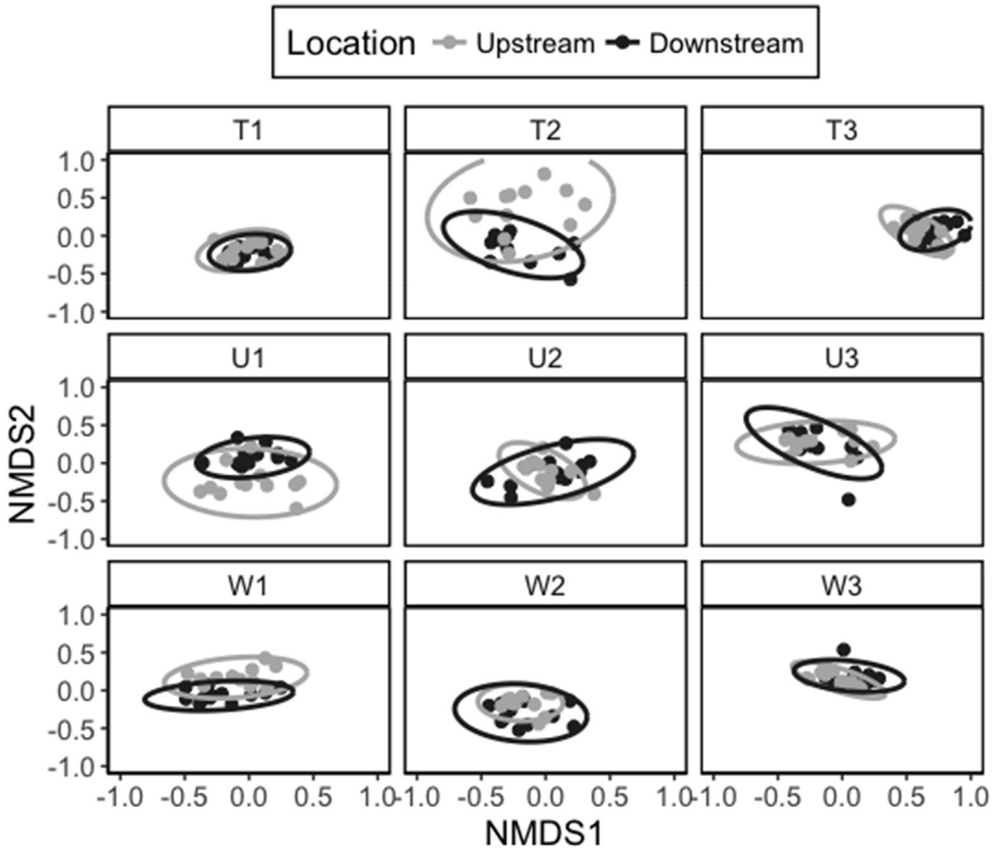

Fig. 3. Multivariate relationships between sites and WwTW discharges. Ellipsoids indicate 95% confidence intervals for groups (upstream and downstream of WwTWs). The total stress value for the NMDS was 0.16, indicating a reasonable fit. Statistical analyses of multivariate data are presented in the text (M-GLM), with community structure variable across sample sites, as well as upstream and downstream of WwTW discharges.

3.4. Food webs and persistent contaminants along an urban gradient

Structural (and functional) characteristics of macroinvertebrate food webs were related to persistent contaminants and urban land cover (Fig. 6). Taxonomic diversity of macroinvertebrate communities reduced significantly in relation to both greater total concentration of PCBs and PBDEs in the tissues of invertebrates and with the level of urban land cover ($R^2 = 0.92$, $F_{2,6} = 46.08$, $p < 0.001$). Taxonomic diversity was related most strongly to contaminant concentrations ($t = -2.93$, $p = 0.026$). Measures of invertebrate functional diversity were also related to both urban land cover and these persistent contaminants. As an example, functional dispersion (FDis), was explained by both urban land cover and levels of persistent contaminants in invertebrates in combination ($R^2 = 0.81$, $F_{2,6} = 18.07$, $p = 0.003$), mostly reflecting the apparent relationship with persistent contaminant concentrations ($t = -2.91$, $p = 0.021$) rather than urban land cover ($t = -1.07$, $p = 0.328$). Finally, food web characteristics were also related to the concentrations of persistent contaminants and urban land cover, for example the mean chain length decreased within increasing levels of PCBs, PBDEs and urban land cover ($R^2 = 0.72$, $F_{2,6} = 7.58$, $p = 0.023$). Further relationships between a wider range of diversity and food web metrics are presented in Appendix S5.

4. Discussion

Although there is evidence of recovery in the UK's urban rivers from the past effects of gross pollution, previous studies have reported only partial recovery for benthic invertebrates (Vaughan and Ormerod, 2012) and fish (Mawle and Milner, 2008). Our data confirm that the structure, functional diversity and food web character of invertebrate communities remain impaired in the urban river systems of South Wales. Urban effects on ionic composition or habitat structure could not be eliminated entirely as an explanation, but relationships between water quality or habitat indices and urban land cover or wastewater discharge in the rivers studied were relatively weak. In contrast, selected persistent contaminants (PCBs and PBDEs) occurred at significantly higher concentrations in invertebrates downstream of urban pollution sources. In combination, these data offer support for the hypothesis that contaminant mixtures, might explain the incomplete recovery of macroinvertebrate food webs from the past effects of gross pollution, though this support is qualified by the possibility that other stressors associated with urban stream systems might also be involved. Our data also add a novel dimension to understanding contaminant effects on river organisms through the indicating potential food webs responses to persistent pollution.

As with all field studies of this type, our results are subject to several caveats. First and most important, the relationships detected between urban land cover, contaminants and macroinvertebrate communities were correlative, and do not necessarily reflect cause-effect links. In particular, urbanisation causes a range of changes in river systems in addition to pollution, for example altering habitat structure, temperature regimes, discharge and night-time light regimes in ways that confound straightforward interpretation (Paul and Meyer, 2001). In this study at least, limited alterations in general water quality (nitrate, phosphate,

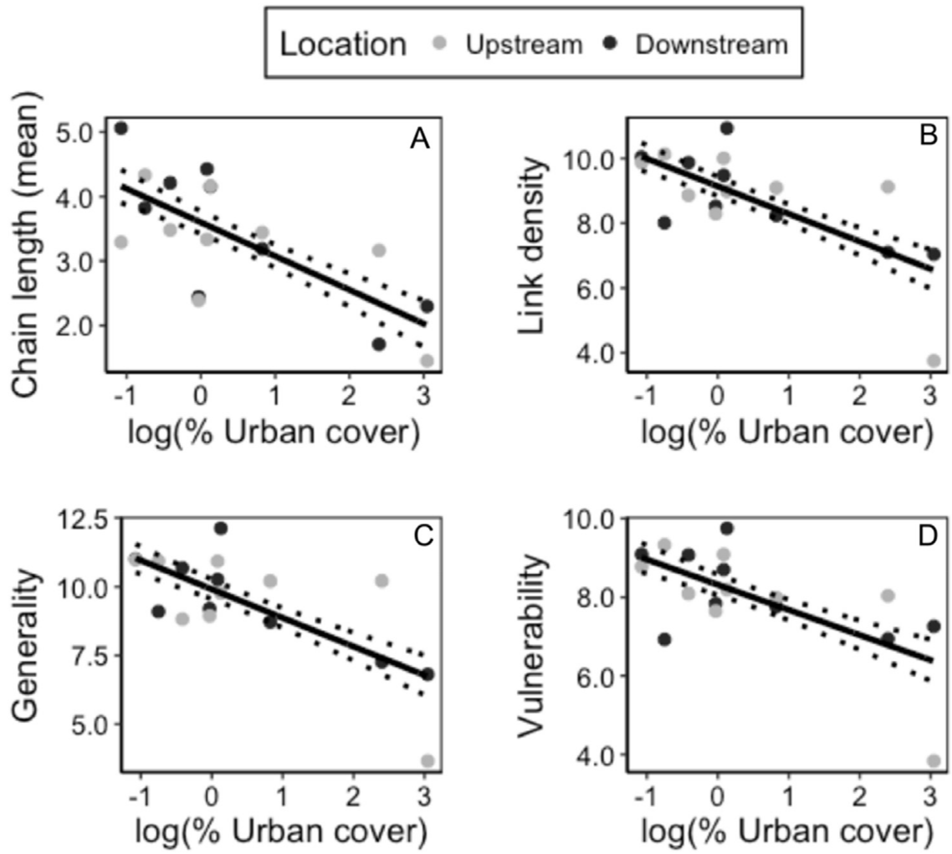

Fig. 4. Relationships between quantitative food web metrics and log percentage urban cover across sample sites. Dotted lines are ±1 standard error. Statistics are provided in text. No significant relationships were observed between food web structure metrics and WwTW discharges.

temperature, EC and TDS) in urban locations reduce the likelihood that the biological effects attributed to persistent contamination were in fact related predominantly to conventional pollution. Further, although we measured just two groups of chemicals (PCBs and PBDEs), these hydrophobic compounds readily enter the benthic habitats of river systems and are likely to interact more strongly with benthic invertebrates than various other contaminants, notably hydrophilic, water-bound contaminants. They are also have long residence times and high bioavailability in the benthic environment (Gaskell et al., 2007). These compounds are also likely to be representative of a larger array of persistent contaminants in urban river systems (Pal et al., 2014). Thus, there is a strong likelihood that effects ascribed here to these two groups in reality relate to a combination effect of wider range of covariate pollutants, e.g. heavy metals, plastics, polycyclic aromatic hydrocarbons and perfluorinated alkyl compounds. A second caveat is that our study used relatively few sites, instead focusing on the detailed parameterisation of biological communities and thus the identification of putative ecological responses to pollution. On one hand this restricts the spatial coverage of findings, yet previous studies operating at broader spatial scales, e.g. national monitoring (e.g. Dyer and Wang, 2002), often compromise on biological detail by limiting metrics to sensitive taxa or univariate metrics of community structure (e.g. Species At Risk index; Munz et al., 2017). Overall, while our data provide an indication of the potential effects of urban pollutants on river food webs, we suggest that the results are interpreted with the above limitations in mind.

The low-flow and mean-flow contribution of wastewater effluent to stream systems in this study (0.5–6.1% and 0.02–1.09%, respectively) initially appear low compared to other published literature (30–50%; Rueda et al., 2002). In part, this reflects the long-standing regulation of sewage volumes relative to the discharge of the rivers that receive them. Moreover, there are good reasons to believe that even these low effluent contributions could still generate ecological effects. Firstly, we calculated the relative contribution of effluent from the individual inputs of WwTWs rather than the total volume of upstream effluent input (e.g. 82% in the River Lea; Harries et al., 1996). Secondly, using mean daily river discharge in the calculation of dilution factors provides conservative estimates of the total effluent contributions (0.02–1.09%) in comparison to low-flow values (0.5–6.1%). This is especially important considering the rapid hydrological response of these piedmont river systems in a region of high rainfall. For example, the range of river discharge recorded (2016–2017) at the gauging station proximal to T1 (River Taff) was 1.54–83.90 $m^3 s^{-1}$ (© Natural Resources Wales and database right. All rights reserved). Thirdly, although the relative contribution of effluent appeared low compared with other studies in dryland regions (e.g. Mediterranean streams), our results are corroborated by work elsewhere that has demonstrated significant effects on river food webs where total effective contributions of effluent averaged 3% (deBruyn et al., 2003). Finally, the relative contribution of effluent is based on discharge volume, hence only provides a crude indication of potential strength of effects which depend also on effluent toxicity, effluent composition by source (e.g. industrial, domestic) and the effectiveness of any treatment processes (Dyer and Wang, 2002). In these same rivers, even with low apparent contributions, effluent contributions to river runoff are sufficient to alter stable isotopic character of freshwater invertebrates, suggesting substantial effects on macro-nutrient fluxes (Morrissey et al., 2013a).

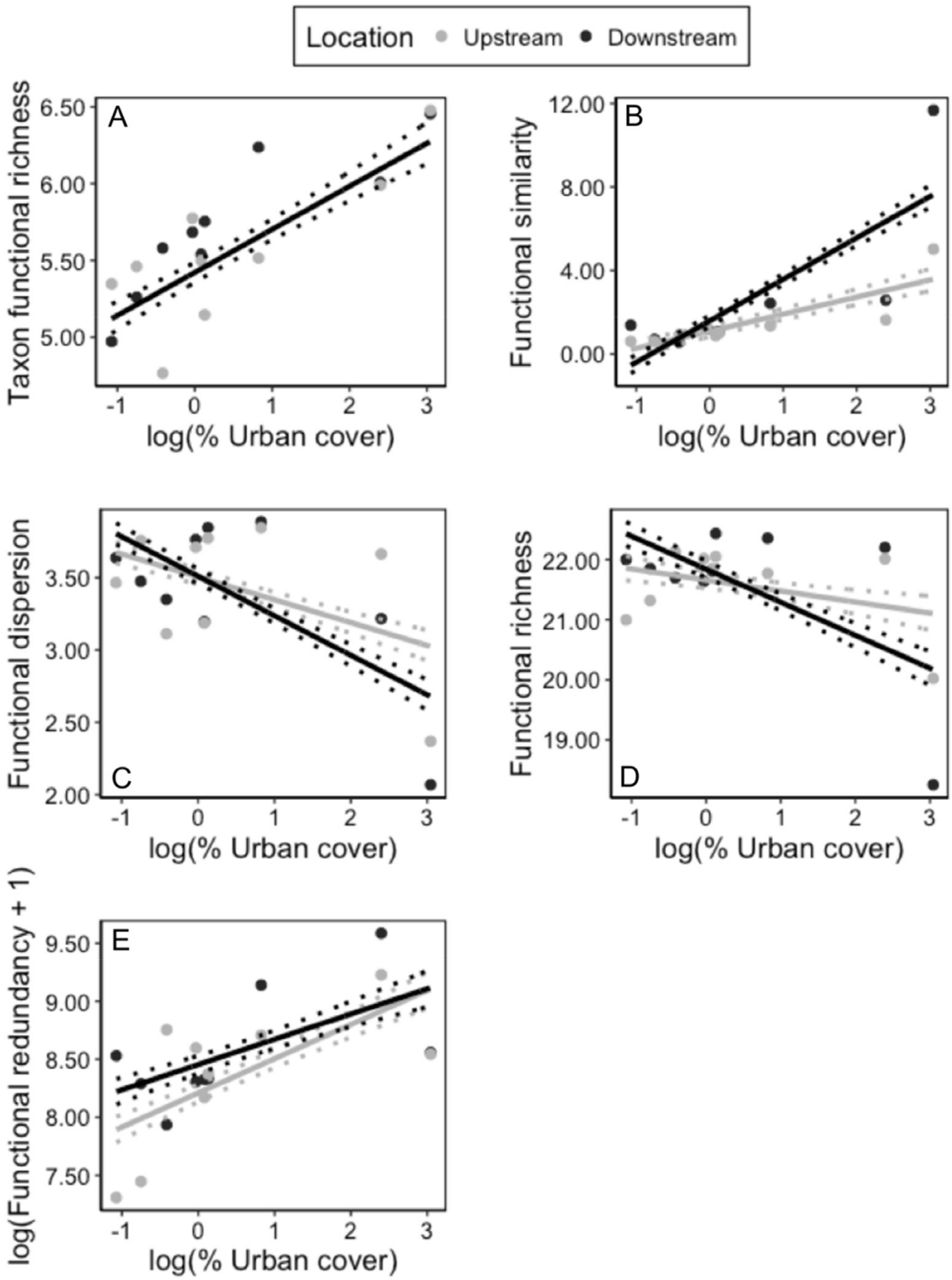

Fig. 5. Relationships between functional diversity metrics, urban land cover and WwTW discharges. Location denotes sites upstream or downstream of WwTW discharges. Dotted lines are ±1 standard error.

Notwithstanding the relatively small proportionate contribution to flow volume, our findings suggest that differences in invertebrate community and food web character in urban landscapes are strongly associated with wastewater discharges and the accompanying higher levels of PCBs and PBDEs contamination. These associations occurred in spite of only minor differences in other measured physicochemical factors that could explain reduced biological diversity in urban river systems, notably water temperature, conductivity, dissolved solids, nitrate, phosphate and habitat character (Vaughan and Ormerod, 2012). While improvements in wastewater treatment have reduced gross pollution problems across urban river systems in England and Wales sufficiently to allow clean water species such as Atlantic salmon (*Salmo salar*; Linnaeus 1758) to recolonise (Mawle and Milner, 2008), changes in invertebrate richness and composition do not yet show full recovery (Maltby and Ormerod, 2011; Vaughan and Ormerod, 2012). Inputs into rivers of both persistent and current-use pollutants in urban areas from general runoff, storm drains, combined sewer overflows and wastewater discharges, therefore, offer a plausible explanation for the limited observed recovery from past pollution. Indeed, previous data from these rivers show that wastewater discharges are sufficient to change the stable isotopic signatures of river organisms, implying the involvement of wastewater in energy and nutrient additions in food webs (Morrissey et al., 2013a). Further to this, the occurrence of persistent organic contaminants in apex predators such as the Eurasian dipper (*Cinclus cinclus*) along

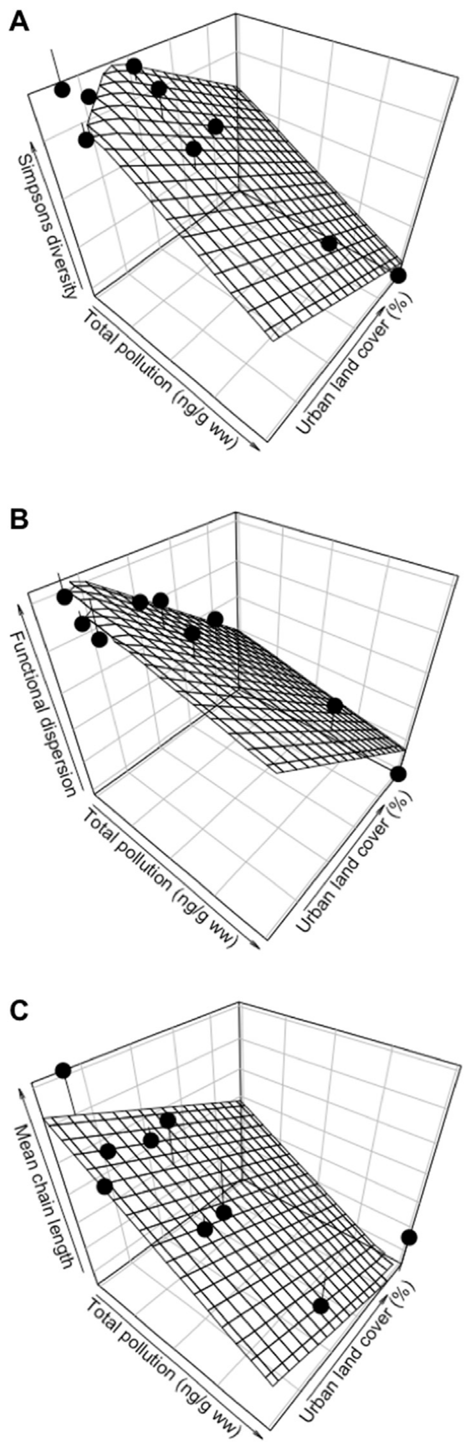

Fig. 6. Relationships between metrics describing macroinvertebrate communities, contaminants (weighted PCBs and PBDEs, ng/g ww) and urban land cover. (A) Taxonomic diversity. (B) Functional dispersion. (C) Mean chain length of food webs. Three-dimensional planes are produced from multiplicative linear regressions reported in the main text.

the same rivers at concentrations that have been implicated in negative ecotoxicological effects (Morrissey et al., 2013b, 2014).

Although the toxicological data for the effects of modern or legacy xenobiotic substances on invertebrates are still scarce (Windsor et al., 2018), based on rudimentary environmental quality standards (EQS_{Biota}) values for PBDEs (European Commission, 2013), the raw concentration data of PBDE congeners (28, 47, 99, 100, 153 and 154) observed in invertebrates herein (0.07−7.61 ng/g ww) are representative of potential ecological effects (>0.0085 ng/g ww; Directive, 2008/105/EU), thus further supporting the observed alterations in invertebrate communities. These risk thresholds, however, are generalised across fish, molluscs, crustaceans and other biota, thus a key question that follows is whether the concentrations PBDEs, PCBs and other urban contaminants, were sufficiently high in invertebrates to cause any ecotoxicological effects that might explain the observed food-web impairment or reduced diversity. Certainly, compared to other studies on similar invertebrate taxa, the levels of both PCBs (0.18−36.28 ng/g ww) and PBDEs (0.08−7.61 ng/g ww), appear similar, if not marginally higher than in other studies in urban river systems; PCBs (1.81−22.07 ng/g ww; Walters et al., 2008) and PBDEs (1.20−13.8 ng/g ww; de Boer et al., 2003). The largest needs overall are for a more complete understanding of the exact array of contaminants present in urban rivers, coupled with ecotoxicological assessments focusing on the effects of urban chemical mixtures under both field and controlled laboratory conditions.

The detection of an interaction between urban land cover and the presence of wastewater discharges further highlights the importance appraising the environmental context in which the effects of pollution occur (see Burdon et al., 2016). In our case, urban land cover and WwTW discharges appeared to act together in reducing biodiversity, while wastewater discharges in less urbanised sites had more restricted effects on the structure and function of invertebrate communities. The higher concentrations of persistent pollutants, nitrate, phosphate, in combination with reduced habitat quality in urban stream systems appeared to alter food web structure and function, with WwTW discharges compounding effects through pollutant addition. The trend observed here contrasts with one case study in which wastewater discharges in Swiss rural stream systems had greater effects − yet this is possibly because pollutant loads in the streams investigated streams were dominated by pesticides from agricultural run-off (Burdon et al., 2016; Munz et al., 2017). Certainly, the structure of invertebrate communities is influenced by pesticides, often from agricultural sources (Beketov et al., 2013). The influence of agricultural pollution and pesticides in the current study, however, cannot be excluded, as these compounds are also emitted from both WwTWs, and other sources, in agricultural regions (Bunzel et al., 2013; Münze et al., 2017). Although the concentration and composition of xenobiotic pollution may vary between river systems in agricultural and urban regions, it is apparent, from this study and others, that the combination of pollution from the wider catchment and WwTW discharges are responsible for generating reductions in the structural and functional diversity of invertebrate communities.

In addition to identifying the potential role for contaminants in slowing the recovery of urban rivers from gross pollution, a novel aspect of our study was the assessment of food-web effects of pollution. Such assessments are infrequent, with studies instead focusing on individual- and population-level responses (Windsor et al., 2018). Our data has revealed a series of potential emergent effects on food webs in response to contamination in urban river systems, including a reduction in connectance and link density that is indicative of food web simplification. Such effects on food webs, although suspected from previous isotope analyses (di Lascio et al., 2013), have not previously been shown. Additionally, we identified how urban pollution could cause a range of functional alterations among invertebrate communities through trait-based analyses. This included reductions in the relative abundance of aerially dispersing taxa at polluted, urbanised sites that, if pronounced, could have implications for prey subsidies to riparian zones through reduced matter and energy transfer (Kautza and Sullivan, 2015). Such effects may in turn impact predators, such as bats, that prey on insects emerging from rivers and can be affected by changes in the prey spectrum available (Abbott et al., 2009).

As well as consequences for riparian organisms dependent on emergent prey, the simplification of aquatic food webs at polluted urban sites also has the potential to affect aquatic apex predators. A range of clean-water vertebrates rely on macroinvertebrate prey in rivers, including salmonid fish (Bell et al., 1994) and river birds that have recently recolonised the UK's recovering urban river systems (Ormerod, 1985; Ormerod and Tyler, 1991; Mawle and Milner, 2008). The observed reductions in the density of several macroinvertebrate taxa in the urban rivers of South Wales (e.g. *Hydropsyche* spp., *Rhyacophila* spp. and *Leuctra* spp.) is likely important for apex predators, for example these taxa would normally form a large component of the diet of the Eurasian dipper (*Cinclus cinclus*; Linnaeus 1758) (Ormerod, 1985). These prey items are nutritionally important for both adults and juveniles, and any reductions in their density in the benthos could carry significant energetic costs (O'Halloran et al., 1990). Any such indirect effects of contamination on prey available to dippers, alongside direct effects generated by the enhanced bioaccumulation of toxic xenobiotic pollutants (Morrissey et al., 2013b), would be consistent with their inferior body condition along urban rivers in South Wales (Morrissey et al., 2014).

5. Conclusion

In conclusion, despite improving water quality and increasing invertebrate richness in urban river systems across the UK over the past 30 years, our data from study sites in South Wales provide evidence that xenobiotic contaminants could offer a potential explanation for the incomplete recovery in the structure and function of biological communities in these same rivers. Simplified macroinvertebrate food webs, alterations in trait character and reduced functional diversity could all have implications for vertebrates that depend on river production, while also offering biological indications of progress towards recovery that are not normally appraised. We suggest there is a need to understand changes like these in more detail, at broader spatial extents, and at sufficient biological resolution to capture emergent ecosystem effects.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: None.

Acknowledgements

This work was supported by a studentship through the GW4+ Doctoral Training Partnership from the Natural Environment Research Council [NE/L002434/] (FMW). Thanks go to Natural Resources Wales for providing water quality data. FMW would also like to thank Heather Carter and Alex Hunter at CEH Lancaster for assistance with chemical analyses. Finally, thanks to the many research assistants for aiding data collection and sample processing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2019.114858.

References

Bersier, L.-F., Banasek-Richter, C., Cattin, M.-F., 2002. Quantitative descriptors of food-web matrices. Ecology 83, 2394–2407. https://doi.org/10.1890/0012-9658(2002)083[2394:QDOFWM]2.0.CO;2.

Raven, P.J., Holmes, N.T.H., Dawson, F.H., Everard, M., 1998. Quality assessment using river habitat survey data. Aquat. Conserv. Mar. Freshw. Ecosystems 8, 477–499. https://doi.org/10.1002/(SICI)1099-0755(199807/08)8:4<477::AID-AQC299>3.0.CO;2-K.

Abbott, I.M., Sleeman, D.P., Harrison, S., 2009. Bat activity affected by sewage effluent in Irish rivers. Biol. Conserv. 142, 2904–2914. https://doi.org/10.1016/J.BIOCON.2009.07.012.

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., Thomaidis, N.S., Xu, J., 2017. Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review. J. Hazard Mater. 323, 274–298. https://doi.org/10.1016/j.jhazmat.2016.04.045.

Bates, D., Maechler, M., Bolker, B., Walker, S., 2015. Fitting linear mixed-effects models using lme4. J. Stat. Softw. 67, 1–48.

Beisel, J.-N., Usseglio-Polatera, P., Thomas, S., Moreteau, J.-C., 1998. Stream community structure in relation to spatial variation: the influence of mesohabitat characteristics. Hydrobiologia 389, 73–88. https://doi.org/10.1023/A:1003519429979.

Beketov, M.A., Kefford, B.J., Schäfer, R.B., Liess, M., 2013. Pesticides reduce regional biodiversity of stream invertebrates. Proc. Natl. Acad. Sci. U.S.A. 110, 11039–11043. https://doi.org/10.1073/pnas.1305618110.

Bell, J.G., Ghioni, C., Sargent, J.R., 1994. Fatty acid compositions of 10 freshwater invertebrates which are natural food organisms of Atlantic salmon parr (Salmo salar): a comparison with commercial diets. Aquaculture 128, 301–313. https://doi.org/10.1016/0044-8486(94)90319-0.

Bester, K., Scholes, L., Wahlberg, C., McArdell, C.S., 2008. Sources and mass flows of xenobiotics in urban water cycles — an overview on current knowledge and data gaps. Water, Air, Soil Pollut. 8, 407–423. https://doi.org/10.1007/s11267-008-9189-3.

Blackburn, M.A., Waldock, M.J., 1995. Concentrations of alkylphenols in rivers and estuaries in England and Wales. Water Res. 29, 1623–1629. https://doi.org/10.1016/0043-1354(94)00340-D.

Brose, U., Cushing, L., Berlow, E.L., Jonsson, T., Banasek-Richter, C., Bersier, L.-F., Blanchard, J.L., Brey, T., Carpenter, S.R., Blandenier, M.-F.C., Cohen, J.E., Dawah, H.A., Dell, T., Edwards, F., Harper-Smith, S., Jacob, U., Knapp, R.A., Ledger, M.E., Memmott, J., Mintenbeck, K., Pinnegar, J.K., Rall, B.C., Rayner, T., Ruess, L., Ulrich, W., Warren, P., Williams, R.J., Woodward, G., Yodzis, P., Martinez, N.D., 2005. Body sizes of consumers and their resources. Ecology 86. https://doi.org/10.1890/05-0379, 2545–2545.

Brosnan, T.M., O'Shea, M.L., 1996. Long-term improvements in water quality due to sewage abatement in the Lower Hudson River. Estuaries 19, 890–900. https://doi.org/10.2307/1352305.

Bunzel, K., Kattwinkel, M., Liess, M., 2013. Effects of organic pollutants from wastewater treatment plants on aquatic invertebrate communities. Water Res. 47, 597–606. https://doi.org/10.1016/J.WATRES.2012.10.031.

Burdon, F.J., Reyes, M., Alder, A.C., Joss, A., Ort, C., Räsänen, K., Jokela, J., Eggen, R.I.L., Stamm, C., 2016. Environmental context and magnitude of disturbance influence trait-mediated community responses to wastewater in streams. Ecol. Evol. 6, 3923–3939. https://doi.org/10.1002/ece3.2165.

Chao, A., Chazdon, R.L., Colwell, R.K., Shen, T.-J., 2005. A new statistical approach for assessing similarity of species composition with incidence and abundance data. Ecol. Lett. 8, 148–159. https://doi.org/10.1111/j.1461-0248.2004.00707.x.

Colborn, T., vom Saal, F.S., Soto, A.M., 1993. Developmental effects of endocrine-disrupting chemicals in wildlife and humans. Environ. Health Perspect. 101, 378–384. https://doi.org/10.2307/3431890.

de Boer, J., Wester, P.G., van der Horst, A., Leonards, P.E.G., 2003. Polybrominated diphenyl ethers in influents, suspended particulate matter, sediments, sewage treatment plant and effluents and biota from The Netherlands. Environ. Pollut. 122, 63–74. https://doi.org/10.1016/S0269-7491(02)00280-4.

deBruyn, A.M., Marcogliese, D.J., Rasmussen, J.B., 2003. The role of sewage in a large river food web. Can. J. Fish. Aquat. Sci. 60, 1332–1344. https://doi.org/10.1139/f03-114.

di Lascio, A., Rossi, L., Carlino, P., Calizza, E., Rossi, D., Costantini, M.L., 2013. Stable isotope variation in macroinvertebrates indicates anthropogenic disturbance along an urban stretch of the river Tiber (Rome, Italy). Ecol. Indicat. 28, 107–114. https://doi.org/10.1016/J.ECOLIND.2012.04.006.

Dray, S., Choler, P., Dolédec, S., Peres-Neto, P.R., Thuiller, W., Pavoine, S., ter Braak, C.J.F., 2014. Combining the fourth-corner and the RLQ methods for assessing trait responses to environmental variation. Ecology 95, 14–21. https://doi.org/10.1890/13-0196.1.

Dudgeon, D., Arthington, A.H., Gessner, M.O., Kawabata, Z.-I., Knowler, D.J., Lévêque, C., Naiman, R.J., Prieur-Richard, A.-H., Soto, D., Stiassny, M.L.J., Sullivan, C.A., 2006. Freshwater biodiversity: importance, threats, status and conservation challenges. Biol. Rev. 81, 163–182. https://doi.org/10.1017/S1464793105006950.

Dyer, S.D., Wang, X., 2002. A comparison of stream biological responses to discharge from wastewater treatment plants in high and low population density areas. Environ. Toxicol. Chem. 21, 1065–1075. https://doi.org/10.1002/etc.5620210524.

Eggen, R.I.L., Hollender, J., Joss, A., Schärer, M., Stamm, C., 2014. Reducing the discharge of micropollutants in the aquatic environment: the benefits of upgrading wastewater treatment plants. Environ. Sci. Technol. 48, 7683–7689.
European Commission, 2013. Directive 2013/39/EU of the European Parliament and of the Council amending directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. J. Eur. Union L 226, 1–17.
Feng, H., Kirk Cochran, J., Lwiza, H., Brownawell, B.J., Hirschberg, D.J., 1998. Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson River. Mar. Environ. Res. 45, 69–88. https://doi.org/10.1016/S0141-1136(97)00025-1.
Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P., Xiao, X., Ran, R., Cheng, F., Peng, X., Wang, Z., Wa Tang, U., 2003. Persistent organic pollutants in environment of the Pearl River Delta, China: an overview. Chemosphere 52, 1411–1422. https://doi.org/10.1016/S0045-6535(03)00477-6.
Gaskell, P.N., Brooks, A.C., Maltby, L., 2007. Variation in the bioaccumulation of a sediment-sorbed hydrophobic compound by benthic macroinvertebrates: patterns and mechanisms. Environ. Sci. Technol. 41, 1783–1789. https://doi.org/10.1021/es061934b.
Gavrilescu, M., Demnerová, K., Aamand, J., Agathos, S., Fava, F., 2015. Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation. Nat. Biotechnol. 32, 147–156. https://doi.org/10.1016/j.nbt.2014.01.001.
Gray, C., Figueroa, D.H., Hudson, L.N., Ma, A., Perkins, D., Woodward, G., 2015. Joining the dots: an automated method for constructing food webs from compendia of published interactions. Food Webs 5, 11–20. https://doi.org/10.1016/j.fooweb.2015.09.001.
Grönroos, M., Heino, J., 2012. Species richness at the guild level: effects of species pool and local environmental conditions on stream macroinvertebrate communities. J. Anim. Ecol. 81, 679–691. https://doi.org/10.1111/j.1365-2656.2011.01938.x.
Gutiérrez-Cánovas, C., Sánchez-Fernández, D., Velasco, J., Millán, A., Bonada, N., 2015. Similarity in the difference: changes in community functional features along natural and anthropogenic stress gradients. Ecology 96, 2458–2466. https://doi.org/10.1890/14-1447.1.
Harding, J.S., Benfield, E.F., Bolstad, P.V., Helfman, G.S., Jones, E.B., 1998. Stream biodiversity: the ghost of land use past. Proc. Natl. Acad. Sci. U.S.A. 95, 14843–14847.
Harries, J.E., Sheahan, D.A., Matthiessen, P., Neall, P., Rycroft, R., Tylor, T., Jobling, S., Routledge, E.J., Sumpter, J.P., 1996. A survey of estrogenic activity in United Kingdom inland waters. Environ. Toxicol. Chem. 15, 1993–2002. https://doi.org/10.1002/etc.5620151118.
Heeb, F., Singer, H., Pernet-Coudrier, B., Qi, W., Liu, H., Longrée, P., Müller, B., Berg, M., 2012. Organic micropollutants in rivers downstream of the megacity Beijing: sources and mass fluxes in a large-scale wastewater irrigation system. Environ. Sci. Technol. 46, 8680–8688.
Hess, A.D., 1941. New limnological sampling equipment. Limnol. Soc. Am. 6, 1–5.
Hudson, L.N., Emerson, R., Jenkins, G.B., Layer, K., Ledger, M.E., Pichler, D.E., Thompson, M.S.A., O'Gorman, E.J., Woodward, G., Reuman, D.C., 2013. Cheddar: analysis and visualisation of ecological communities in R. Methods Ecol. Evol. 4, 99–104. https://doi.org/10.1111/2041-210X.12005.
Igbinosa, E.O., Okoh, A.I., 2009. Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving watershed in a typical rural community. Int. J. Environ. Sci. Technol. 6, 175–182. https://doi.org/10.1007/BF03327619.
Jaccard, P., 1908. Nouvelles recherches sur la distribution florale. Bull. Société Vaudoise des Sci. Nat. 44, 223–270.
JNNC, 2010. Handbook for Phase 1 Habitat Survey - a Technique for Environmental Audit. JNNC, Peterborough, UK.
Jobling, S., Nolan, M., Tyler, C.R., Brighty, G., Sumpter, J.P., 1998. Widespread sexual disruption in wild fish. Environ. Sci. Technol. 32, 2498–2506. https://doi.org/10.1021/es9710870.
Karickhoff, S.W., Brown, D.S., Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13, 241–248. https://doi.org/10.1016/0043-1354(79)90201-X.
Kautza, A., Sullivan, S.M.P., 2015. Shifts in reciprocal river-riparian arthropod fluxes along an urban-rural landscape gradient. Freshw. Biol. 60, 2156–2168. https://doi.org/10.1111/fwb.12642.
Kenkel, N.C., Orloci, L., 1986. Applying metric and nonmetric multidimensional scaling to ecological studies: some new results. Ecology 67, 919–928. https://doi.org/10.2307/1939814.
Krein, A., Keßler, S., Meyer, B., Pailler, J.-Y., Guignard, C., Hoffmann, L., 2013. Concentrations and loads of dissolved xenobiotics and hormones in two small river catchments of different land use in Luxembourg. Hydrol. Process. 27, 284–296. https://doi.org/10.1002/hyp.9209.
Maltby, E., Ormerod, S.J., 2011. Freshwaters - openwaters, wetlands and floodplains. In: The UK National Ecosystem Assessment Technical Report. UNEP WCMC, Cambridge, U.K, pp. 295–360.
Marra, G., Wood, S.N., 2011. Practical variable selection for generalized additive models. Comput. Stat. Data Anal. 55, 2372–2387. https://doi.org/10.1016/j.csda.2011.02.004.
Mawle, G.W., Milner, N.J., 2008. The return of Salmon to cleaner rivers - England and Wales. In: Mills, D. (Ed.), Salmon at the Edge. Blackwell Publishing, Oxford, UK, pp. 186–199.
Morrissey, Boldt, A., Mapstone, A., Newton, J., Ormerod, S.J., 2013a. Stable isotopes as indicators of wastewater effects on the macroinvertebrates of urban rivers. Hydrobiologia 700, 231–244. https://doi.org/10.1007/s10750-012-1233-7.
Morrissey, Stanton, D.W.G., Pereira, M.G., Newton, J., Durance, I., Tyler, C.R., Ormerod, S.J., 2013b. Eurasian dipper eggs indicate elevated organohalogenated contaminants in urban rivers. Environ. Sci. Technol. 47, 8931–8939. https://doi.org/10.1021/es402124z.
Morrissey, C.A., Stanton, D.W.G., Tyler, C.R., Pereira, M.G., Newton, J., Durance, I., Ormerod, S.J., 2014. Developmental impairment in eurasian dipper nestlings exposed to urban stream pollutants. Environ. Toxicol. Chem. 33, 1315–1323. https://doi.org/10.1002/etc.2555.
Moss, B., 2008. Water pollution by agriculture. Philos. Trans. R. Soc. Lond. B Biol. Sci. 363, 659–666. https://doi.org/10.1098/rstb.2007.2176.
Munz, N.A., Burdon, F.J., de Zwart, D., Junghans, M., Melo, L., Reyes, M., Schönenberger, U., Singer, H.P., Spycher, B., Hollender, J., Stamm, C., 2017. Pesticides drive risk of micropollutants in wastewater-impacted streams during low flow conditions. Water Res. 110, 366–377. https://doi.org/10.1016/J.WATRES.2016.11.001.
Münze, R., Hannemann, C., Orlinskiy, P., Gunold, R., Paschke, A., Foit, K., Becker, J., Kaske, O., Paulsson, E., Peterson, M., Jernstedt, H., Kreuger, J., Schüürmann, G., Liess, M., 2017. Pesticides from wastewater treatment plant effluents affect invertebrate communities. Sci. Total Environ. 599–600, 387–399. https://doi.org/10.1016/J.SCITOTENV.2017.03.008.
Ormerod, S.J., 1985. The diet of breeding Dippers Cinclus cinclus and their nestlings in the catchment of the River Wye, mid-Wales: a preliminary study by faecal analysis. Ibis 127, 316–331. https://doi.org/10.1111/j.1474-919X.1985.tb05073.x.
Ormerod, S.J., Tyler, S.J., 1991. Exploitation of prey by a river bird, the dipper Cinclus cinclus (L.), along acidic and circumneutral streams in upland Wales. Freshw. Biol. 25, 105–116. https://doi.org/10.1111/j.1365-2427.1991.tb00477.x.
Owens, P.N., Walling, D.E., Carton, J., Meharg, A.A., Wright, J., Leeks, G.J.L., 2001. Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialized drainage basins. Sci. Total Environ. 266, 177–186. https://doi.org/10.1016/S0048-9697(00)00729-4.
O'Halloran, J., Gribbin, S.D., Tyler, S.J., Ormerod, S.J., 1990. The ecology of dippers Cinclus cinclus (L.) in relation to stream acidity in upland Wales: time-activity budgets and energy expenditure. Oecologia 85, 271–280. https://doi.org/10.1007/BF00319413.
Pal, A., He, Y., Jekel, M., Reinhard, M., Gin, K.Y.-H., 2014. Emerging contaminants of public health significance as water quality indicator compounds in the urban water cycle. Environ. Int. 71, 46–62. https://doi.org/10.1016/J.ENVINT.2014.05.025.
Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. Annu. Rev. Ecol. Systemat. 32, 333–365. https://doi.org/10.1146/annurev.ecolsys.32.081501.114040.
Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Res. 72, 3–27. https://doi.org/10.1016/j.watres.2014.08.053.
Phillips, P.J., Chalmers, A.T., Gray, J.L., Kolpin, D.W., Foreman, W.T., Wall, G.R., 2012. Combined sewer overflows: an environmental source of hormones and wastewater micropollutants. Environ. Sci. Technol. 46, 5336–5343.
Pitt, R., Field, R., Lalor, M., Brown, M., 1995. Urban stormwater toxic pollutants: assessment, sources, and treatability. Water Environ. Res. 67, 260–275.
Purdom, C.E., Hardiman, P.A., Bye, V.V.J., Eno, N.C., Tyler, C.R., Sumpter, J.P., 1994. Estrogenic effects of effluents from sewage treatment works. Chem. Ecol. 8, 275–285. https://doi.org/10.1080/02757549408038554.
R Core Team, 2015. R: A Languages and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.
Reid, A.J., Carlson, A.K., Creed, I.F., Eliason, E.J., Gell, P.A., Johnson, P.T.J., Kidd, K.A., MacCormack, T.J., Olden, J.D., Ormerod, S.J., Smol, J.P., Taylor, W.W., Tockner, K., Vermaire, J.C., Dudgeon, D., Cooke, S.J., 2018. Emerging threats and persistent conservation challenges for freshwater biodiversity. Biol. Rev. Early View. https://doi.org/10.1111/brv.12480.
Relyea, R.A., 2005. The impact of insecticides and herbicides on the biodiversity and productivity of aquatic communities. Ecol. Appl. 15, 618–627. https://doi.org/10.1890/03-5342.
Rueda, J., Camacho, A., Mezquita, F., Hernández, R., Roca, J.R., 2002. Effects of episodic and regular sewage discharges on the water chemistry and macroinvertebrate fauna of a Mediterranean stream. Water. Air. Soil Pollut. 140, 425–444.
Ruxton, G.D., Beauchamp, G., 2008. Some suggestions about appropriate use of the Kruskal–Wallis test. Anim. Behav. 76, 1083–1087. https://doi.org/10.1016/j.anbehav.2008.04.011.
Schäfer, S., Buchmeier, G., Claus, E., Duester, L., Heininger, P., Körner, A., Mayer, P., Paschke, A., Rauert, C., Reifferscheid, G., Rüdel, H., Schlechtriem, C., Schröter-Kermani, C., Schudoma, D., Smedes, F., Steffen, D., Vietoris, F., 2015. Bioaccumulation in aquatic systems: methodological approaches, monitoring and assessment. Environ. Sci. Eur. 27, 5. https://doi.org/10.1186/s12302-014-0036-z.
Schulz, R., 2004. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution. J. Environ. Qual. 33, 419–448. https://doi.org/10.2134/jeq2004.4190.
Schwarzenbach, R.P., Egli, T., Hofstetter, T.B., von Gunten, U., Wehrli, B., 2010. Global water pollution and human health. Annu. Rev. Environ. Resour. 35, 109–136. https://doi.org/10.1146/annurev-environ-100809-125342.
Scullion, J., Edwards, R.W., 1980. The effects of coal industry pollutants on the macroinvertebrate fauna of a small river in the South Wales coalfield. Freshw. Biol. 10, 141–162. https://doi.org/10.1111/j.1365-2427.1980.tb01189.x.

Segner, H., Caroll, K., Fenske, M., Janssen, C.R., Maack, G., Pascoe, D., Schäfers, C., Vandenbergh, G.F., Watts, M., Wenzel, A., 2003. Identification of endocrine-disrupting effects in aquatic vertebrates and invertebrates: report from the European IDEA project. Ecotoxicol. Environ. Saf. 54, 302–314. https://doi.org/10.1016/S0147-6513(02)00039-8.

Simpson, E.H., 1949. Measurement of diversity. Nature 163. https://doi.org/10.1038/163688a0, 688–688.

Tachet, H., Bournaud, P., Usseglio-Polatera, P., 2002. Invertébrés d'Eau Douce, Second cor. CNRS éditions, Paris.

Taebi, A., Droste, R.L., 2004. Pollution loads in urban runoff and sanitary wastewater. Sci. Total Environ. 327, 175–184. https://doi.org/10.1016/j.scitotenv.2003.11.015.

ter Braak, C.J.F., Peres-Neto, P., Dray, S., 2017. A critical issue in model-based inference for studying trait-based community assembly and a solution. PeerJ 5, e2885. https://doi.org/10.7717/peerj.2885.

Thomas, R., Lello, J., Medeiros, R., Pollard, A., Seward, A., Smith, J., Vafidis, J., Vaughan, I., 2015. Data Analysis with R Statistical Software: A Guidebook for Scientists. Eco-Explore, Newport, UK.

Tyler, C.R., Jobling, S., Sumpter, J.P., 1998. Endocrine disruption in wildlife: a critical review of the evidence. Crit. Rev. Toxicol. 28, 319–361.

van Loosdrecht, M.C.M., Brdjanovic, D., 2014. Water treatment. Anticipating the next century of wastewater treatment. Science (80-.) 344, 1452–1453. https://doi.org/10.1126/science.1255183.

Vaughan, I.P., Ormerod, S.J., 2012. Large-scale, long-term trends in British river macroinvertebrates. Glob. Chang. Biol. 18, 2184–2194. https://doi.org/10.1111/j.1365-2486.2012.02662.x.

Ver Hoef, J.M., Peterson, E.E., Clifford, D., Shah, R., 2014. SSN: an R package for spatial statistical modeling on stream networks. J. Stat. Softw. 56, 1–45. https://doi.org/10.18637/jss.v056.i03.

Violle, C., Enquist, B.J., McGill, B.J., Jiang, L., Albert, C.H., Hulshof, C., Jung, V., Messier, J., 2012. The return of the variance: intraspecific variability in community ecology. Trends Ecol. Evol. 27, 244–252. https://doi.org/10.1016/j.tree.2011.11.014.

Walsh, C.J., 2000. Urban impacts on the ecology of receiving waters: a framework for assessment, conservation and restoration. Hydrobiologia 431, 107–114. https://doi.org/10.1023/A:1004029715627.

Walters, D.M., Fritz, K.M., Johnson, B.R., Lazorchak, J.M., McCormick, F.H., 2008. Influence of trophic position and spatial location on polychlorinated biphenyl (PCB) bioaccumulation in a stream food web. Environ. Sci. Technol. 42, 2316–2322. https://doi.org/10.1021/es0715849.

Wang, Y., Naumann, U., Wright, S.T., Warton, D.I., 2012. Mvabund - an R package for model-based analysis of multivariate abundance data. Methods Ecol. Evol. 3, 471–474. https://doi.org/10.1111/j.2041-210X.2012.00190.x.

Watts, M.M., Pascoe, D., Carroll, K., 2003. Exposure to 17α-ethinylestradiol and bisphenol A - effects on larval moulting and mouthpart structure of Chironomus riparius. Ecotoxicol. Environ. Saf. 54, 207–215. https://doi.org/10.1016/S0147-6513(02)00029-5.

Windsor, F.M., Ormerod, S.J., Tyler, C.R., 2018. Endocrine disruption in aquatic systems: up-scaling research to address ecological consequences. Biol. Rev. 93, 626–641. https://doi.org/10.1111/brv.12360.

Zhou, J.L., Zhang, Z.L., Banks, E., Grover, D., Jiang, J.Q., 2009. Pharmaceutical residues in wastewater treatment works effluents and their impact on receiving river water. J. Hazard Mater. 166, 655–661. https://doi.org/10.1016/j.jhazmat.2008.11.070.

Zimmerman, J.B., Mihelcic, J.R., Smith, J., 2008. Global stressors on water quality and quantity. Environ. Sci. Technol. 42, 4247–4254.

Zuur, A.F., Leno, E.N., Smith, G.M., 2007. Analysing Ecological Data. Springer, New York, USA.

Zuur, A.F., Leno, E.N., Elphick, C.S., 2010. A protocol for data exploration to avoid common statistical problems. Methods Ecol. Evol. 1, 3–14. https://doi.org/10.1111/j.2041-210X.2009.00001.x.